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Kinetics of Stereochemical Rearrangements for Mixed β -Diketonate Complexes of Aluminum(III)

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Kinetic parameters for the intramolecular environmental interchange of nonequivalent terminal groups on the like ligands of the following mixed β -diketonate complexes of aluminum(III) have been determined by nmr spectroscopy: $\text{Al}(\text{acac})(\text{hfac})_2$, $\text{Al}(\text{acac})_2(\text{hfac})$, and $\text{Al}(\text{acac})_2(\text{bzbz})$, where acac = acetylacetonate, hfac = hexafluoroacetylacetonate, and bzbz = dibenzoylmethanate. The rates of terminal CF_3 group exchange for $\text{Al}(\text{hfac})_2(\text{acac})$ were studied in benzene, dichloromethane, and nitrobenzene; the activation energies (kcal/mol) and entropies (eu) at 25° are, respectively, 19.0 ± 1.3 and 2.9 ± 4.2 in C_6H_6 , 21.3 ± 0.7 and 10.7 ± 2.2 in CH_2Cl_2 , and 19.5 ± 0.6 and 5.7 ± 1.9 in $\text{C}_6\text{H}_5\text{NO}_2$. For CH_3 group exchange in $\text{Al}(\text{acac})_2(\text{hfac})$ in dichloromethane solution, $E_a = 18.4 \pm 0.7$ kcal/mol and $\Delta S^\ddagger_{25^\circ} = 10.0 \pm 2.4$ eu, and for $\text{Al}(\text{acac})_2(\text{bzbz})$ in *o*-dichlorobenzene, $E_a = 22.0 \pm 0.6$ kcal/mol and $\Delta S^\ddagger_{25^\circ} = 0.9 \pm 1.5$ eu. The results are evaluated in terms of a bond-rupture mechanism in which one metal-oxygen bond ruptures to give a five-coordinate intermediate.

Introduction

A variety of intramolecular mechanisms have been proposed for the stereochemical rearrangement or racemization of octahedral complexes containing three bidentate ligands. The mechanisms may be classified according to two general types: (1) twisting processes in which the metal-ligand bonds twist without bond rupture to give a trigonal-prismatic intermediate or transition state¹⁻⁵ and (2) bond-rupture processes in which one metal-ligand bond ruptures to give a five-coordinate intermediate.⁶⁻⁸ It is well established that tris- β -diketonate complexes of the group III metals undergo rapid intramolecular stereochemical rearrangements,⁷⁻¹⁰ and some evidence has been presented which indicates that the rearrangements occur *via* a bond-rupture mechanism. For example, the observed increase in rate with increasing solvent polarity for the isomerization of $\text{Al}(\text{tfac})_3$ ¹¹ suggests that charge separation occurs in the transition state.⁷ Also, the difference in activation energies for the interchange of nonequivalent terminal methyl groups in $\text{Ga}(\text{acac})_2(\text{bzbz})$ and the more labile $\text{Ga}(\text{acac})_2(\text{hfac})$ is in accord with the expected relative magnitudes of the mean thermochemical gallium-oxygen bond energies for the two complexes.¹⁰ In order to test these mechanistic implications further we have investigated the solvent dependence of the activation parameters for terminal CF_3 group exchange in $\text{Al}(\text{acac})(\text{hfac})_2$ and the kinetics of CH_3 group exchange for $\text{Al}(\text{acac})_2(\text{hfac})$. The rearrangement of $\text{Al}(\text{acac})_2(\text{bzbz})$ is also reported, and the labilities of analogous

aluminum and gallium β -diketonates are compared. This work represents the first accurate determination of activation parameters for stereochemical rearrangement processes of aluminum β -diketonates.

Experimental Section

Preparation of Complexes.—Aluminum(III) acetylacetonate was prepared from aluminum isopropoxide and acetylacetonate in a manner similar to that described previously for preparation of other aluminum(III) β -diketonates.¹² The compound was recrystallized from benzene-hexane and dried *in vacuo* at 80° for 0.5 hr; mp 194–195°, lit.¹³ mp 196.4°. Aluminum(III) hexafluoroacetylacetonate was synthesized and purified according to the method described by Morris, Moshier, and Sievers;¹⁴ mp 73.0–73.5°, lit.¹⁴ mp 73–74°. Aluminum(III) dibenzoylmethanate (mp 307–310°) was prepared by using the method described for the gallium(III) analog.¹⁵ Although $\text{Al}(\text{bzbz})_3$ has been reported previously,¹⁶ no criteria for estimating purity were given. Therefore, the compound was analyzed. *Anal.* Calcd for $\text{Al}(\text{C}_{15}\text{H}_{11}\text{O}_2)_3$: C, 77.58; H, 4.77; Al, 3.87. Found: C, 77.80; H, 4.90; Al, 4.05.

Mixed β -diketonate complexes in the $\text{Al}(\text{acac})_3$ – $\text{Al}(\text{hfac})_3$ and $\text{Al}(\text{acac})_3$ – $\text{Al}(\text{bzbz})_3$ systems were generated in solution by equilibrating mixtures of the parent complexes at 60 and 79°, respectively. The approximate time required for equilibration was 20 hr for the $\text{Al}(\text{acac})_3$ – $\text{Al}(\text{hfac})_3$ system and 10 hr for the $\text{Al}(\text{acac})_3$ – $\text{Al}(\text{bzbz})_3$ system. The maximum equilibrium molar fraction of $\text{Al}(\text{acac})(\text{hfac})_2$ was obtained when the fraction of total ligand present as acetylacetonate, f_{acac} , was 0.33. The maximum molar fractions of $\text{Al}(\text{acac})_2(\text{hfac})$ and $\text{Al}(\text{acac})_2(\text{bzbz})$ were obtained at $f_{\text{acac}} = 0.67$. For all equilibrium mixtures, the total solute concentration was ca. 0.20 M. No attempt was made to isolate the mixed-ligand complexes since within the time period necessary to complete the nmr studies, the isolated mixed complex would only disproportionate and regenerate the complexes present in the original equilibrium mixture.

Solvents.—All solvents used in the kinetic studies were reagent grade. Benzene, *o*-dichlorobenzene, and dichloromethane were dried over calcium hydride. Nitrobenzene was purified and dried as described previously.¹⁷ After being dried, the solvents were handled under a dry nitrogen atmosphere.

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- (11) The following abbreviations are used throughout: tfac, tiffuoroacetylacetonate; acac, acetylacetonate; bzbz, dibenzoylmethanate; hfac, hexafluoroacetylacetonate.

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Nmr Spectra.—Proton (60.0 MHz) and fluorine (56.4 MHz) magnetic resonance spectra were obtained on a Varian A 56/60 D analytical spectrometer equipped with a V-6040 temperature controller. Temperatures were determined by recording the chemical shift difference between the proton resonances of either methanol (low temperatures) or ethylene glycol (high temperatures).¹⁸ Magnetic field sweeps were calibrated by the audio-frequency side-band technique.

Typical ¹⁹F nmr spectra for Al(acac)(hfac)₂ in the region of slow exchange and in the region of exchange below and above the coalescence temperature are shown in Figure 1. The tempera-

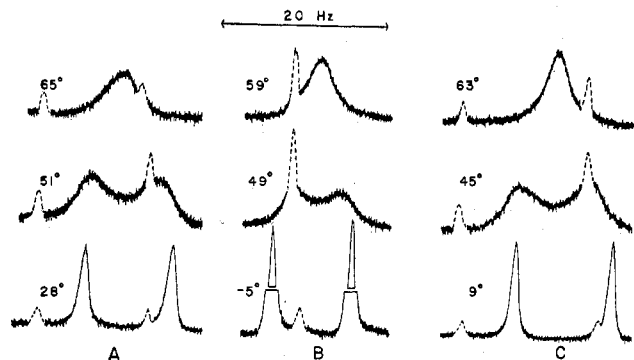


Figure 1.—The ¹⁹F nmr spectra (56.4 MHz) for Al(acac)(hfac)₂ in (A) benzene, (B) dichloromethane, and (C) nitrobenzene. Dashed lines are resonances due to Al(acac)₂(hfac) and Al(hfac)₃.

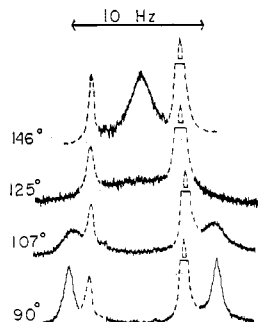


Figure 2.—Methyl proton nmr spectra (60.0 MHz) for Al(acac)₂(bz bz) in *o*-dichlorobenzene. Dashed lines are resonances due to Al(acac)(bz bz)₂ and Al(acac)₃.

ture dependence of the methyl proton nmr spectrum of Al(acac)₂(bz bz) in *o*-dichlorobenzene is illustrated in Figure 2. Methyl proton spectra for the third compound studied, Al(acac)₂(hfac) in dichloromethane solution, are qualitatively similar to those reported previously for the analogous gallium complex in the region of exchange.¹⁰

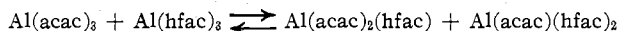
Nmr Line-Shape Parameters.—Three line-shape parameters were used in comparing the observed nmr spectra with spectra computed for various terminal group lifetimes. Below the coalescence temperature the spectra were compared with respect to the observed frequency separation between the two resonance components, and the ratio of the maximum to central minimum amplitudes. Above coalescence the line width at half-maximum amplitude was used. At each temperature four copies of the spectrum were recorded, and the line-shape parameters were averaged. The reliability of the line-shape parameter method for comparing observed and calculated spectra has been verified in a previous study of related mixed β -diketonates of gallium.¹⁰

The calculated nmr spectra have been described previously.¹⁰ Values of the transverse relaxation times for the methyl protons and fluorine atoms in the mixed-ligand complexes in the region of exchange were assumed to be equal to the values found for Al-

(acac)₃ and Al(hfac)₃ over the same temperature range. These assumptions were supported by the fact that the line widths of the mixed-ligand complexes in the regions of very slow and very fast exchange were equal within experimental error (± 0.05 Hz) to the line widths of the parent complexes. The relaxation time for the methyl protons was temperature independent in *o*-dichlorobenzene over the range 140–161° but temperature dependent in dichloromethane over the range –6–7.4°. These two temperature ranges correspond to the regions of exchange for Al(acac)₂(bz bz) and Al(acac)₂(hfac), respectively. Over the temperature range corresponding to the regions of exchange for Al(acac)(hfac)₂ (40–78°), the transverse relaxation time for the methyl fluorine atoms was independent of both the temperature and the nature of the solvent. With the exception of Al(acac)₂(hfac) in dichloromethane, all of the mixed-ligand complexes exhibited an appreciable temperature dependence for $\delta\nu$, the frequency separation between the resonance components in absence of exchange. Therefore, values of $\delta\nu$ at temperatures in the region of exchange were obtained by linear least-squares extrapolation of the temperature dependence of the frequency separation in the region of slow exchange. Similar methods for obtaining values of relaxation times and values of $\delta\nu$ have been described in detail for mixed β -diketonate complexes of gallium(III).¹⁰

Results and Discussion

The mixed aluminum- β -diketonate complexes of interest in this study exist in solution in equilibrium with their parent complexes. For the acetylacetonate-hexafluoroacetylacetonate system the overall equilibrium may be written as



An analogous equilibrium applies to the acetylacetonate-dibenzoylmethanate system. The former system deviates markedly from a random statistical distribution of ligands, favoring the mixed-ligand complexes,⁸ whereas the latter system behaves more nearly statistically.¹⁹ Thus the precision of an nmr study of environmental interchange for the two sets of non-equivalent terminal groups on a mixed complex depends not only on a suitable chemical shift difference between the resonance components in absence of exchange (>1 Hz) but also on the adequate resolution of these lines from those of the other compounds in the equilibrium mixture. The ¹⁹F nmr lines (56.4 MHz) of Al(acac)(hfac)₂ were well resolved in benzene, dichloromethane, and nitrobenzene (*cf.* Figure 1), and adequate resolution of the methyl proton resonances (60.0 MHz) of Al(acac)₂(hfac) and Al(acac)₂(bz bz) was achieved in dichloromethane and *o*-dichlorobenzene, respectively. No attempt was made to determine the rates of phenyl group interchange for Al(acac)(bz bz)₂, because of the complexity of the phenyl proton resonances.

The ¹⁹F nmr line-shape parameters for the exchange of nonequivalent CF₃ groups in Al(acac)(hfac)₂ in three different solvents are given in Table I along with the parameter τ , where $\tau = \tau_A/2 = \tau_B/2$ and τ_A and τ_B are the mean lifetimes of the CF₃ groups in the two environments. Similar data are presented in Tables II and III for the exchange of terminal methyl groups in Al(acac)₂(hfac) and Al(acac)₂(bz bz), respectively. Arrhenius activation energies, E_a , and frequency factors, A , for the exchange processes were determined in

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TABLE I
¹⁹F NMR LINE-SHAPE PARAMETERS AND VALUES OF τ FOR
 Al(acac)(hfac)₂ IN VARIOUS SOLVENTS

Temp, °C	$\delta\nu$, ^a Hz	$\delta\nu_e$, ^b Hz	r ^c	W^* , ^d Hz	$10^2\tau$, sec
C ₆ H ₆ Solvent					
48.4	9.70	9.00	2.65	...	6.05
49.1	9.67	8.30	2.10	...	5.10
50.5	9.62	8.20	1.78	...	4.60
51.2	9.59	8.15	1.87	...	4.70
65.0	9.07	5.40	1.50
67.4	8.97	3.30	0.930
70.7	8.85	2.90	0.815
73.9	8.73	2.31	0.625
78.4	8.56	1.92	0.490
CH ₂ Cl ₂ Solvent					
39.9	7.88	7.34	3.76	...	10.2
40.5	7.86	7.26	3.35	...	9.40
44.0	7.76	6.70	2.44	...	7.50
45.4	7.71	6.68	1.71	...	5.95
49.2	7.60	4.20	1.13	...	3.82
53.1	7.48	6.66	2.56
58.9	7.30	3.36	1.40
60.7	7.25	2.99	1.24
63.1	7.18	2.45	1.02
67.1	7.06	1.88	0.690
69.1	6.99	1.60	0.530
70.3	6.96	1.60	0.530
C ₆ H ₅ NO ₂ Solvent					
39.7	10.13	^e	3.49	...	6.90
42.2	10.01		2.32	...	5.30
45.1	9.88		1.67	...	4.20
46.6	9.80		1.33	...	3.56
54.4	9.43		...	6.30	1.62
58.3	9.24		...	4.42	1.21
59.3	9.19		...	4.10	1.13
60.1	9.16		...	3.70	1.02
62.2	9.05		...	3.02	0.830
62.5	9.04		...	3.32	0.930
62.7	9.03		...	3.00	0.820
66.2	8.86		...	2.25	0.580
67.4	8.80		...	2.14	0.550
68.6	8.75		...	2.00	0.490
72.4	8.56		...	1.80	0.430

^a Frequency separation between the resonance components in absence of exchange. ^b Observed frequency separation. ^c Ratio of the maximum to central minimum signal intensities below coalescence. ^d Full line width at half-maximum amplitude for the time-averaged resonance above coalescence. ^e Values of $\delta\nu_e$ in C₆H₅NO₂ are uncertain due to overlap with Al(hfac)₃ resonance.

the usual way from the least-squares straight line of the $\log k$ vs. $1/T$ plots, where $k = (2\tau)^{-1}$ is the first-order rate constant for exchange. Typical plots are shown in Figure 3 for Al(acac)(hfac)₂. The Arrhenius kinetic parameters are summarized in Table IV along with extrapolated values of k and calculated values of ΔS^\ddagger at 25°. Included in Table IV are kinetic parameters for terminal group exchange for similar gallium compounds. It is to be noted that reasonable experimental uncertainties in the relaxation times (T_2) for Al(acac)(hfac)₂ and Al(acac)₂(bzbz) propagate systematic errors in E_a and ΔS^\ddagger which are smaller than the estimates of random error at the 95% confidence level. Because of the rather small frequency separation between the resonance components for Al(acac)₂(hfac), however, uncertainties in T_2 for this latter complex can

TABLE II
 METHYL PROTON NMR LINE-SHAPE PARAMETERS^a AND
 VALUES OF τ FOR Al(acac)₂(hfac) IN DICHLOROMETHANE

Temp, °C	$\delta\nu_e$, Hz	r	W^* , Hz	$10^2\tau$, sec
-10.4	2.84	3.24	...	41.9 ^b
-5.7	2.45	2.15	...	22.1
-2.8	2.23	1.44	...	14.7
-0.2	1.86	1.17	...	11.2
2.7	3.62	8.06
4.1	2.96	6.49
4.5	2.97	6.57
6.0	2.53	4.91
8.1	1.86	3.96
8.1	1.89	4.19

^a Definitions of all parameters are the same as those given in Table I. ^b All values of τ were calculated for $\delta\nu = 3.11$ Hz.

TABLE III
 METHYL PROTON NMR LINE-SHAPE PARAMETERS^a AND
 VALUES OF τ FOR Al(acac)₂(bzbz) IN *o*-DICHLOROBENZENE

Temp, °C	$\delta\nu$, Hz	$\delta\nu_e$, Hz	W^* , Hz	$10^2\tau$, sec
106.9	11.07	10.72	...	8.15 ^b
110.0	10.99	10.30	...	5.87 ^b
142.1	10.11	...	2.79	0.639
145.8	10.01	...	2.20	0.526
147.8	9.95	...	2.15	0.489
150.5	9.88	...	1.70	0.383
152.9	9.82	...	1.55	0.343
156.6	9.71	...	1.35	0.266

^a Definitions of all parameters are the same as those given in Table I. ^b These values of τ below coalescence were obtained by fitting only $\delta\nu_e$.

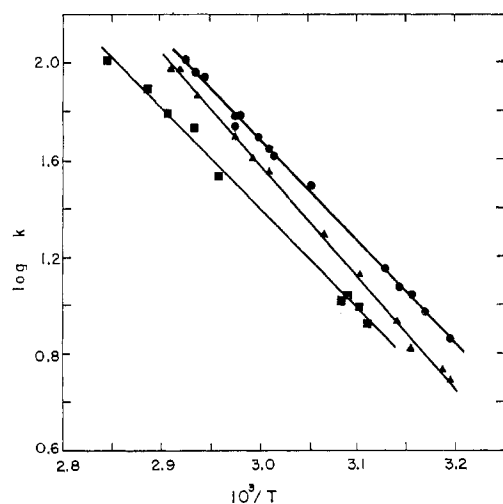


Figure 3.—Arrhenius plots for the interchange of nonequivalent CF₃ groups in Al(acac)(hfac)₂ in benzene (■—■), dichloromethane (▲—▲), and nitrobenzene (●—●) solutions.

propagate systematic errors in the activation parameters which are comparable to the estimates of random error quoted in Table IV.

A comparison of τ values for Al(acac)(hfac)₂ (cf. Table I) indicates that the stereochemical lability of the compound increases with increasing solvent polarity in the order benzene < dichloromethane < nitrobenzene.²⁰ Using six solvents of different polarity, Fay and Piper⁷

(20) The dielectric constants of the solvents used in this study are as follows: C₆H₆ at 60°, 2.20; *o*-C₂H₄Cl₂ at 25°, 7.4; CH₂Cl₂ at 20°, 9.08; C₆H₅NO₂ at 40°, 32.3. The data were taken from E. W. Washburn, Ed., "International Critical Tables," Vol. 6, McGraw-Hill, New York, N. Y., 1929, p 81 ff, and A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. VII, 2nd ed, Interscience, New York, N. Y., 1955, p 182.

TABLE IV
KINETIC PARAMETERS FOR THE INTERCHANGE OF NONEQUIVALENT TERMINAL GROUPS IN MIXED
 β -DIKETONATES OF ALUMINUM(III) AND GALLIUM(III)

Compound	Solvent	k_{25° , sec ⁻¹	E_a , kcal/mol	Log A	$\Delta S^\ddagger_{25^\circ}$, eu
Al(acac)(hfac) ₂	C ₆ H ₆	8.4×10^{-1} ^a	19.0 ± 1.3 ^b	3.87 ± 0.82	2.9 ± 4.2
	CH ₂ Cl ₂	8.6×10^{-1}	21.3 ± 0.7	15.55 ± 0.45	10.7 ± 2.2
	C ₆ H ₅ NO ₂	1.5	19.5 ± 0.6	14.47 ± 0.41	5.7 ± 1.9
Al(acac) ₂ (hfac)	CH ₂ Cl ₂	8.0×10^1	18.4 ± 0.7	15.41 ± 0.53	10.0 ± 2.4
Al(acac) ₂ (bzbz)	<i>o</i> -C ₆ H ₄ Cl ₂	2.2×10^{-3}	22.0 ± 0.6	13.43 ± 0.33	0.9 ± 1.5
Ga(acac) ₂ (hfac) ^c	CH ₂ Cl ₂	7.7×10^2	15.3 ± 1.2	14.07 ± 1.01	3.9 ± 4.6
Ga(acac) ₂ (bzbz) ^c	C ₆ H ₆	7.7×10^{-2}	20.2 ± 3.2	13.72 ± 2.0	2.2 ± 9.3

^a All values of k_{25° are extrapolated values. ^b All errors are estimated at the 95% confidence level. ^c The kinetic parameters for these compounds were computed from the data in ref 10 by using the temperatures given by the Van Geet equations¹⁸ for methanol and ethylene glycol nmr thermometers; the previously reported kinetic parameters, which agree within experimental error with those reported here, were based on the thermometer calibration charts supplied by Varian Associates.

have observed a similar solvent dependence for the rate of isomerization of Al(tfac)₃. Although they could not determine directly the activation energies for the isomerization, it was suggested that the general decrease in activation free energy with increasing solvent polarity was due to a lowering of the activation energy as a result of greater charge separation and greater solvation in the transition state. Greater solvation of the transition state was believed to be more consistent with a bond-rupture mechanism than a twisting mechanism, because in the former mechanism the charge separation in the transition state is greater than that in the ground state due to the presence of the partially charged uncoordinated carbonyl group. The importance of solvation effects in the transition state is not confirmed by the activation energies obtained here for the stereochemical rearrangement of Al(acac)(hfac)₂ (cf. Table IV). The activation energy is in fact 2.3 ± 1.5 kcal/mol larger in dichloromethane than in the less polar solvent benzene. The greater lability of the complex in dichloromethane in the region of exchange is due to an activation entropy which is 7.8 ± 4.7 eu larger than that in benzene. In benzene and nitrobenzene the activation energies and entropies are equal within experimental error. If a bond-rupture mechanism does indeed operate in the rearrangement of Al(acac)(hfac)₂, as is indicated by the magnitudes of the activation entropies (see below), then the lack of a solvent dependence for E_a among the three solvents investigated may be due to solvation effects in the ground state which approximately parallel those in the transition state.

The relative rates of terminal group exchange for Al(acac)(hfac)₂ and the related molecule Al(acac)₂(hfac) differ appreciably. In dichloromethane solution the extrapolated value of the first-order rate constant at 25° is two orders of magnitude larger for Al(acac)₂(hfac) than for Al(acac)(hfac)₂. The data in Table IV indicate that the difference in stereochemical labilities is due to a difference of 2.9 ± 1.0 kcal/mol in activation energies; the activation entropies are equal within experimental error. It has been previously pointed out¹⁰ that hexafluoroacetylacetonate is expected to be a much weaker donor than a nonfluorinated β -diketonate. If we hypothesize a bond-rupture mechanism, it would not be unreasonable to suggest that both Al(acac)(hfac)₂ and Al(acac)₂(hfac) rearrange *via* rupture of a bond be-

tween aluminum and a donor oxygen on hexafluoroacetylacetonate. The origin of the small difference in activation energies for the two molecules is not clear, but one should expect the energy required to break the same type of metal-oxygen bond in two similar molecules to differ depending on the nature of the other ligands bound to the metal atom.

The interchange of nonequivalent methyl group environments on Al(acac)₂(bzbz) is considerably slower than terminal group exchange for both of the mixed acetylacetonate-hexafluoroacetylacetonate complexes. It is noteworthy that the activation energy for Al(acac)₂(bzbz) in *o*-C₆H₄Cl₂ is 3.6 ± 0.9 kcal/mol larger than that for Al(acac)₂(hfac) in dichloromethane. This difference in activation energies could be due to differences in solvation effects, as judged by the range of activation energies for Al(acac)(hfac)₂ at the extreme 95% confidence level estimates of error. Even in the absence of solvation effects, however, a bond-rupture mechanism would predict Al(acac)₂(bzbz) to have the larger activation energy, because of the expected difference in donor strengths of fluorinated and nonfluorinated ligands.

The data in Table IV make possible an evaluation of the relative stereochemical labilities of analogous mixed β -diketonate complexes of aluminum and gallium. Both Ga(acac)₂(hfac) and Ga(acac)₂(bzbz) undergo terminal group exchange faster than their corresponding aluminum derivatives. A comparison of the kinetic parameters for the rearrangement of the M(acac)₂(hfac) complexes in dichloromethane indicates that the activation energy is at least 1.7 kcal/mol lower for the gallium derivative. This result is consistent with either a bond-rupture or twisting mechanism. If a bond-rupture mechanism operates, then the activation energy should be lower for the gallium complex because the mean Ga-O bond energy is appreciably smaller than the mean Al-O bond energy.²¹ On the other hand, a twisting mechanism would predict the same result because of lower ligand-ligand repulsive energies in the transition state for the larger gallium ion.

Perhaps the most cogent evidence in favor of a bond-rupture rather than a twist mechanism for the stereochemical rearrangement of group III metal β -diketonates lies in the magnitudes of the frequency factors.

It has been suggested¹ that a twist mechanism should give rise to a very low frequency factor and a corresponding large entropy loss in the transition state because of the expected low probability for distribution of the activation energy into the appropriate vibrational modes. Accordingly, the low frequency factors of 10^{4-16} and 10^{-4-8} sec⁻¹ for racemization of tris(biguanidinium)cobalt(III), $\text{Co}(\text{bigH})_3^{3+}$, in aqueous solution and $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ in the solid state, respectively, have prompted the assignment of twist mechanisms for these rearrangement processes.^{1,22} By way of comparison, the frequency factors for racemization of $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ and $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ in aqueous solution, where bond-rupture mechanisms probably operate,²³⁻²⁵ are $10^{7.2-23}$ and $10^{14.5}$ sec⁻¹,²⁶ respectively.^{26a} It is also known that $\text{Fe}(\text{phen})_3^{2+}$ racemizes, in part, by an intramolecular path and that a twisting mechanism apparently operates as the rigid structure of the 1,10-phenanthroline ligand precludes a bond-rupture process.²⁷ In con-

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(26a) NOTE ADDED IN PROOF.—Frequency factors in the range $10^{14.7-10^{15.8}}$ sec⁻¹ have been found recently for the isomerization and racemization of cis and trans isomers of tris(5-methylhexane-2,4-dionato)cobalt(III) [J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970)] and cobalt(III) benzoylacetonate [A. Y. Girgis and R. C. Fay, *ibid.*, **92**, 7061 (1970)] in chlorobenzene solution where bond-rupture mechanisms most probably operate.

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trast to the apparent large entropy loss for twisting $\text{Co}(\text{bigH})_3^{3+}$ and $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$, a large entropy gain is associated with the intramolecular racemization of $\text{Fe}(\text{phen})_3^{2+}$ ($\Delta S^\ddagger_{25^\circ} = 21$ eu). In this latter case it has been suggested²⁸ that twisting is preceded by excitation of Fe(II) from a low-spin to a high-spin state and consequent expansion of the coordination sphere of the metal ion; the entropy gain was attributed to a greater degree of freedom of the ligands in the excited state. Although an expansion process may cause the magnitude of the frequency factor for twisting a tris chelate of a low-spin d^6 metal ion to be comparable to that expected for a bond-rupture mechanism, no such expansion process is possible for d^0 metal ion complexes. Therefore, the frequency factors for rearrangement of the group III metal β -diketonates listed in Table IV are believed to be indicative of a bond-rupture mechanism. Frequency factors much smaller than those obtained here have been reported by Fortman and Sievers⁸ for the rearrangement of other mixed aluminum(III) β -diketonates, but these low values are not believed to be reliable, for reasons given elsewhere.¹⁰

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The Two-Electron Inner-Sphere Reduction of Chloropentaammineplatinum(IV) Ion by Aquochromium(II) Ion

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A two-electron inner-sphere reaction is required to account for the stoichiometry and kinetics of the reduction of $\text{Pt}(\text{NH}_3)_5\text{Cl}^{3+}$ by Cr^{2+} . In perchloric acid solutions of pH 0–2 the final chromium(III) products are equivalent amounts of CrCl^{2+} and Cr^{3+} , but at lower acidities appreciable quantities of dimeric $(\text{CrOH})_2^{4+}$ are formed. The rapid and complex absorbance changes observed by stopped-flow spectrophotometry are interpreted as the second-order redox reaction with a rate constant of $5 \times 10^4 M^{-1} \text{sec}^{-1}$ at 25° followed by slower reactions of chromium(III) intermediates. These intermediates have not been completely characterized.

Introduction

The aquochromium(II) ion has been extremely important in the elucidation of oxidation–reduction mechanisms of metal complexes. By exploiting the substitution-inert property of the oxidized Cr(III) product, Taube and Myers² were able to demonstrate that the

reduction of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ proceeds by an inner-sphere activated complex accompanied by ligand transfer of the chlorine from cobalt to chromium, producing CrCl^{2+} . Subsequently, many other studies³ have examined the details of the inner-sphere redox mechanism.

Ardon and Plane⁴ have shown that various oxidations

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